J. Phys. Chem. **1995,** *99,* 9316–9324

ARTICLES

Substituent Effects on Torsional Barriers: *p*-Methoxy- and *p*-Methoxy-*p*′-methyl-*trans*-stilbene

Sonja S. Siewert and Lee H. Spangler*

Department of Chemistry, Montana State University, Bozeman, Montana 59717

Received: January 11, 1995; In Final Form: April 6, 1995[⊗]

Jet-cooled fluorescence excitation spectra and selected single vibronic level dispersed fluorescence spectra are presented for *p*-methoxy-*trans*-stilbene and *p*-methoxy-*p*′-methyl-*trans*-stilbene. Two stable conformers of the methoxy group are evident in the spectra and are distinguishable on the basis of the difference in their ring torsional frequencies. The lower frequency conformer is the better electron donor. Methoxy substitution lowers the S_1 barrier to internal rotation of the methyl group to ~100 cm^{-1} compared to 150 cm^{-1} for *p*-methyl-*trans*-stilbene. The two methoxy conformers have measurably different S_1 barriers. The better donor has the lower barrier, consistent with previous work on *p*-amino-*p*′-methyl-*trans*-stilbene. The spectra also provide evidence of coupling between the ring and methyl torsions and show that methoxy substitution modifies the ring torsional potential energy surface as well.

Introduction

Recent work in this laboratory has investigated the effect of remote substitution on the barrier to methyl internal rotation in *p*-amino-*p*′-methyl-*trans*-stilbene.[1] The S_1 barrier to methyl internal rotation was determined to be $V_3' = 55$ cm^{-1}, nearly a factor of 3 lower than the reported $V_3' = 150$ cm^{-1} barrier in the parent compound, *p*-methyl-*trans*-stilbene.[2] This dramatic reduction in barrier caused by amino substitution 10 atoms away clearly indicates that the π electron system plays a role in the origin of methyl barriers.[3–6]

This work seeks to solidify this model by investigating a substituent of different character which not only is a weaker donor but also possesses an asymmetry about the substituent axis. Because of the complexity of the *p*-methoxy-*p*′-methyl-*trans*-stilbene (MoMeS) spectrum, we will also present the *p*-methoxystilbene (MoS) and *p*-methyl-stilbene (MeS) spectra for comparison purposes.

Experimental Section

The jet apparatus utilizes a General Valve Series 9 pulsed nozzle which sprays into a six in. nominal 6-way cross evacuated by a Varian VHS-6 diffusion pump. Samples were heated to 110–130 °C and entrained in 0.2–7 bar helium. The jet is crossed at 90° by the beam from a Lumonics Hyperdye 300 dye laser (0.07 cm^{-1} resolution) which is pumped with a Lumonics HY750 Nd:YAG laser at a 20 Hz repetition rate. DCM dye was used to acquire the spectra and was frequency doubled in BBO. The emission was collected with a Melles Griot REM 014 ellipsoidal reflector and focused onto the cathode of an EMI 9813QB photomultiplier tube. The resulting signal was fed to an SRS250 boxcar integrator, digitized, and stored on a computer. Laser power was monitored by using a rhodamine 590 solution as a quantum counter and detecting the dye emission with a photomultiplier tube. The excitation spectra presented are an average of three scans, corrected for laser power variation and taken at a resolution of 0.15 cm^{-1}. For the dispersed fluorescence experiments, the emission was once again collected with the ellipsoidal reflector and then focused onto the 100 μm slit of a Spex 0.5 m monochromator with a 3600 line/mm grating. The dispersed fluorescence spectra were acquired by taking an average of ten 2–6 min exposures with a Princeton Instruments liquid nitrogen cooled CCD detection system (1024 × 256 26 μm pixel CCD chip). This gave a linear dispersion of 0.0144 nm/pixel and a final resolution of ≈1.41 cm^{-1} per pixel in this wavelength region. *p*-Methoxy-*trans*-stilbene was obtained from Sigma and used without further purification. *p*-Methoxy-*p*′-methyl-*trans*-stilbene was prepared as follows: One equivalent of the Arbusov product $CH_3{-}C_6H_4{-}CH_2{-}P{=}O(OEt)_2$ was added to 2 equiv of NaH in DME. One equivalent of *p*-anisaldehyde was added, and the mixture was refluxed at 70 °C for 30 min. The reaction was quenched with water, and the resulting crystals were recrystallized twice in ethanol and dried with an overall yield of ≈75%. The *p*-methoxy-*p*′-methyl-*trans*-stilbene has a melting point of 158 °C and was characterized using ^{1}H-NMR and FTIR.

Results and Interpretation

***p*-Methoxy-*trans*-Stilbene.** The jet-cooled fluorescence excitation spectrum of methoxystilbene is presented in Figure 1. Many of the low-frequency transitions can be readily assigned by analogy with *trans*-stilbene (tS).[7,8] These include 36_0^2 at 55.4 cm^{-1}, 37_0^2 at 91.5 cm^{-1}, and 25_0^1 at 171.4 cm^{-1} (compared to 70, 95, and 198 cm^{-1}, respectively, in tS) as well as their combinations (see Table 1). It should be noted that the tS assignments used differ from those most recently published[9] for reasons stated previously.[1] The modes are numbered according to QCFF-PI calculations performed by Warshel,[10] and the assigned bands exhibit dispersed fluorescence spectra very similar to those for the analogous transitions in tS.[7,8] Perhaps the most striking feature of the spectrum is the intense peak at 267 cm^{-1}, for which there is no analog in tS. We assign this

---

* Author to whom correspondence should be addressed. E-mail: uchls@msu.oscs.montana.edu.

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1995.

0022-3654/95/2099-9316$09.00/0

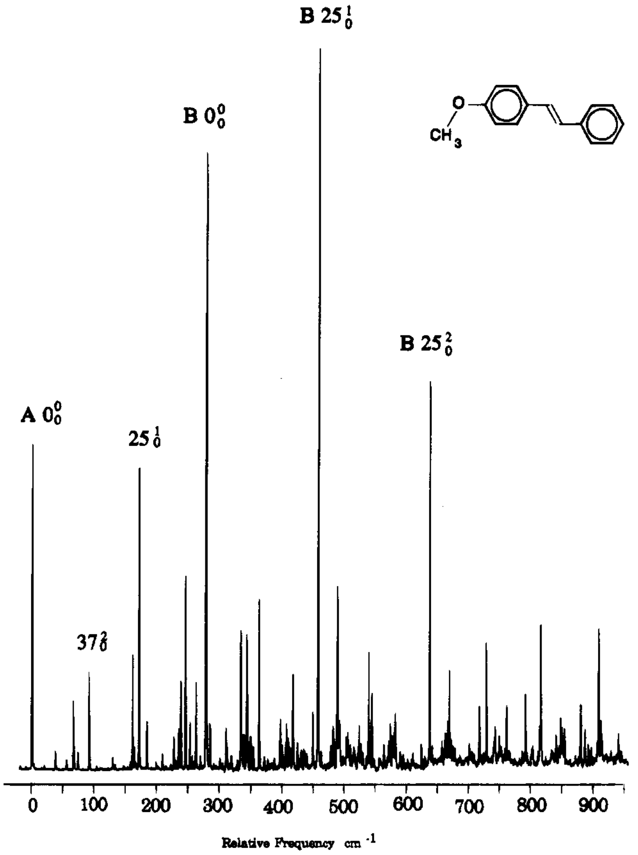

Figure 1. Fluorescence excitation spectrum of *p*-methoxy-*trans*-stilbene (MoS). Two stable conformations of the methoxy group are evident and are marked as A and B.

peak as the origin of a second conformer on the basis of the following evidence: (1) There is no strong transition at 2 × 267 cm^{-1}, as would be expected if this were a vibronic peak built on the first origin. (2) Two origins, spaced ~70 cm^{-1} apart, were observed by Bernstein and co-workers in the related molecules, 1,4-dimethoxybenzene and 1-methoxy-3-methylbenzene.[11] (3) The dispersed fluorescence (DF) spectrum from this peak has origin-like character. (4) AMPAC calculations using the AM1 Hamiltonian predict two stable conformers (both planar). Thus, we conclude that there are two planar conformers, with the OCH$_3$ syn and anti with respect to the carbon–carbon double bond. For reasons to be addressed in the Discussion section, we suspect the lower frequency origin to be due to the syn conformer.

Figure 2 aligns the second (B) origin under the first (A), so the spectra of the two conformers can be compared (keeping in mind that higher frequency vibronic peaks of the A conformer extend into the B conformer's spectrum). This comparison reveals differences in the frequencies for ν_{37}, ν_{25}, and ν_{24} (see Figure 3 for representations of these modes in tS). Dispersed fluorescence from the origins (Figure 4) and 25_0^1 for each conformer reveals a difference in the ν_{25}'' frequency with A:25_1 and B:25_1 having frequencies of 178 and 193 cm^{-1}, respectively. Since ν_{25} is the most Franck–Condon active mode, it appears in the DF spectrum from all transitions and can be used to assign a given vibronic peak as belonging to a specific conformer.

In addition to the frequency differences, ν_{24} and ν_{25} display a notable relative intensity difference between the two conformers which is evident in both the excitation spectra and DF spectra with ν_{24}'' appearing strongly for A and barely evident in emission for B. The larger Franck–Condon distribution for the A conformer lowers the relative intensity of the origin band, and the integrated intensities of the two conformer spectra may be quite similar. Therefore, the lower intensity of the A origin should not necessarily be interpreted as a population difference. The amount of ν_{25} character in the DF from A:24_0^1 and the congested nature of that spectrum suggest that there may also be Duchinski rotation between the 24 and 25 coordinates for the A conformer.

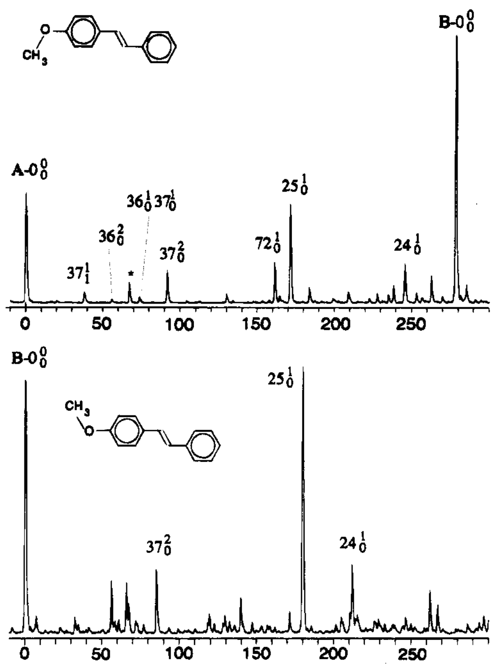

Figure 2. Comparison of the low-frequency portion of the FE spectra for the two conformers of MoS. Note the lower 37_0^2 and higher 25_0^1 frequencies for the B conformer (bottom). The starred transition is believed to be a ring torsional level given allowed character via the methoxy modification of the ring torsional surface (see the Discussion section and Figure 11).

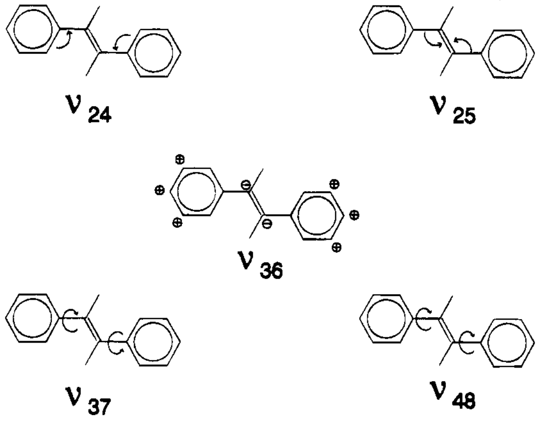

Figure 3. Low-frequency normal modes of *trans*-stilbene, after Warshel.[10]

Figure 5 shows eight of the DF spectra acquired for *p*-methoxystilbene. Both A-37_0^2 and B-37_0^2 show the signature low-frequency progressions in even quanta ν_{37}'' first observed by Ito and co-workers in tS.[7] The emission from 25_0^1 for both conformers exhibits little or no intensity in 25_1 and strong 25_2, 25_3, and 25_4 peaks, as expected when exciting one quantum of a Franck–Condon active mode with intensity comparable to that of the origin. With the aid of dispersed emission spectra and the previous work on stilbenes, most of the assignments in Tables 1 and 2 can be made in a straightforward manner.

However, there are some exceptions. The B-$25_0^1 37_0^2$ combination band should appear with moderate intensity at 264.7 cm^{-1} but was not observed. Instead a doublet with peaks at 261.7

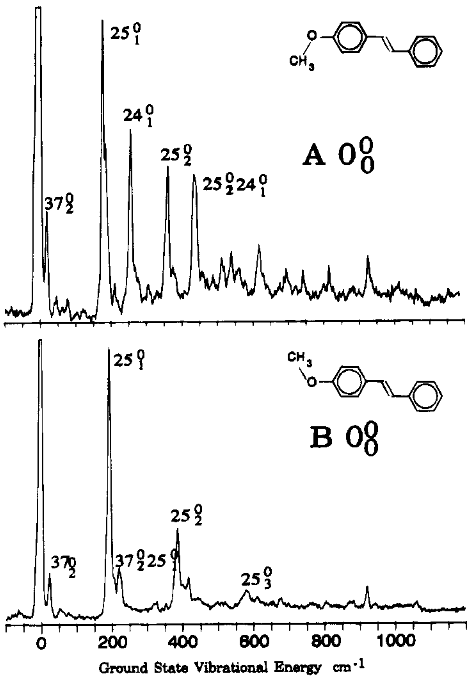

Figure 4. Dispersed fluorescence from the two conformer origins of MoS. The conformers display different S_0 ν_{25} frequencies as in the excited state. The A conformer has significant Franck–Condon activity in ν_{24} while the B conformer does not.

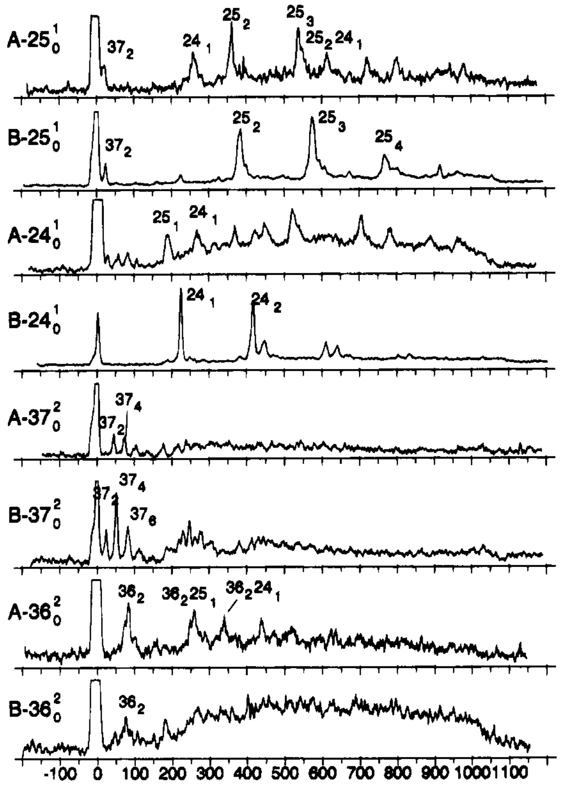

Figure 5. Selected single vibrational level fluorescence spectra used to help assign the excitation spectrum of MoS.

and 267.1 cm^{-1} appears (Figure 6). Dispersed emission from both of these transitions displays activity in ν_{37}'', ν_{25}'', and a 285 cm^{-1} mode, indicating a likely Fermi resonance between $25^1_0 37^2_0$ and an unassigned mode with an approximate frequency of 265 cm^{-1} in S_1 and 285 cm^{-1} in S_0.

The transitions appearing at A + 67 cm^{-1} and B + 67.2 cm^{-1} and 58.3 cm^{-1} in Figure 2 have no analogs in *trans*-stilbene. Possible assignments include the torsion of the methoxy group, torsion of the methyl group in the methoxy, or a methoxy bend. These would seem to be supported by appearance of a similar frequency transition in the anisoles as reported by Bernstein and co-workers.[11] However, preliminary work on *p*-hydroxy-*trans*-stilbene performed in our laboratory indicates transitions at nearly identical frequencies. Owing to the substantial mass differences between OH and OCH₃, it seems unlikely that functional group vibrations for these two substituents would have nearly identical frequencies. We suspect these transitions are due to ring motion; the methoxy group apparently modifies the ring torsional potential energy surface as well.

TABLE 1: S_1 Vibrational Level Assignments for the A and B Conformers of *p*-Methoxy-*trans*-stilbene[a]

	A conformer		B conformer	
assignment	freq (cm^{-1})	relative intensity	freq (cm^{-1})	relative intensity
0^0_0	30 744.1	1.0	31 022.6	1.0
37^1_1	37.8	hb	34.1	hb
36^2_0	55.4	0.08	60.0	0.07
X, ring tors?	67.0	0.23	58.3	0.22
			67.2	0.21
$36^1_0 37^1_0$	73.8	0.09	72.3	0.06
37^2_0	91.5	0.34	85.2	0.27
36^4_0	112.1	0.06	210.0	0.03
37^3_1	129.8	hb	118.8	hb
?	133.8	0.06		
$36^2_0 37^2_0$	146.8	0.06	119.0	0.03
?	157.8	0.08	152.4	0.05
72^1_0	161.2	0.40		
$37^3_0 36^1_0$	164.7	0.11	218	0.04
25^1_0	171.4	0.90	179.5	1.05
37^4_0	183.9	0.19	171.0	0.10
$37^1_1 25^1_0$	209.2	hb		
$37^2_0 37^3_1$	222.6	hb		
$25^1_0 36^2_0$	227.8	0.15	239.5	0.05
$36^1_0 37^1_0 72^1_0$	235.5	0.13		
X + 25^1_0	238.4	0.21		
24^1_0	245.8	0.39	211.8	0.29
$72^1_0 37^2_0$	253.1	0.15		
$25^1_0 37^2_0$	262.8	0.29	261.7	0.19
			267.1	0.14
$37^1_1 24^1_0$	285.4	hb		
$37^3_1 25^1_0$	301.5	hb		
X + 24^1_0	312.8	0.15		
$25^1_0 36^2_0 37^2_0$	318.3	0.11		
72^2_0	319.6	0.08		
$72^1_0 25^1_0$	334.3	0.16		
25^2_0	344.0	0.32	358.9	.58
$25^1_0 37^4_0$	355.3	0.13	351	.04
$24^1_0 72^1_0$	407.0	0.15		
$25^1_0 24^1_0$	419.3	0.29	391.5	.17
24^2_0	293.4	0.24	424.8	.06
25^3_0	516.4	0.12	539.9	.24
$25^2_0 24^1_0$			570.7	.14

[a] Origin frequencies are reported as absolute (±15 cm^{-1}). Other frequencies are relative to the respective origin. hb denotes hot band.

TABLE 2: Ground State S_0 Low-Frequency Vibrational Assignments (Expressed as cm^{-1} above the Vibrationless Level) for *p*-Methoxystilbene

	24^0_1	25^0_1	36^0_2	37^0_2
p-methyl-*trans*-stilbene		200	114	19
p-methoxy-*trans*-stilbene A	258	178	82	21
B	222	193	74	24
p′-methoxy-*p*-methyl-*trans*-stilbene A	247	165		
B	216	174		

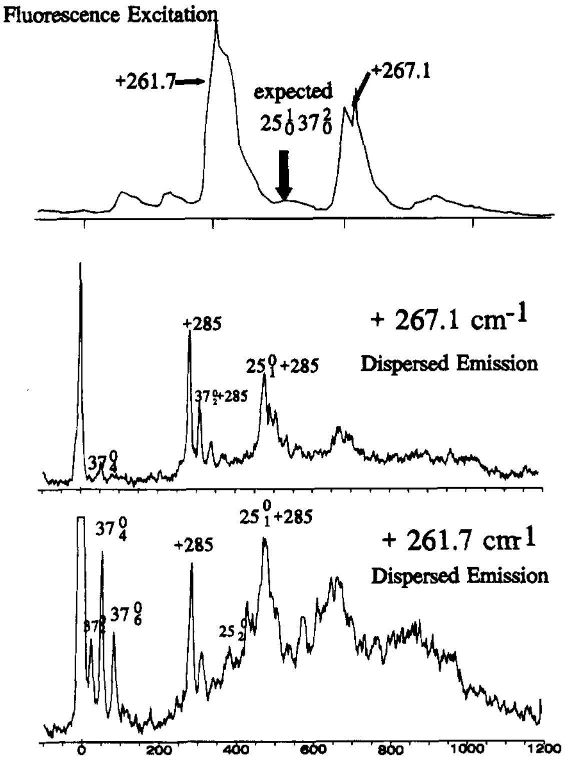

Figure 6. Illustration of the Fermi resonance between B:$25^1_0 37^2_0$ and an unknown transition with ~265 cm^{-1} frequency in the S_1 state of methoxystilbene. Dispersed emission from both transitions displays activity in ν_{25}, ν_{37}, and a mode of ~285 cm^{-1} frequency, which would appear to be the S_0 frequency of the unknown transition.

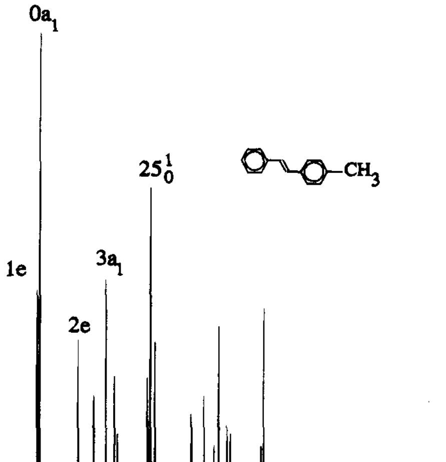

Figure 7. Fluorescence excitation spectrum of *p*-methyl-*trans*-stilbene. The starred transition is assigned as $37^1_0$1e; one quantum of the ring torsion made allowed by combination with the methyl torsion.

***p*-Methyl-*trans*-stilbene.** The excitation spectrum of *p*-methyl-*trans*-stilbene (MeS), previously published,[2] is shown in Figure 7, primarily for comparison purposes. Methyl torsional transitions, easily recognized by their absence in the *trans*-stilbene spectrum, appear at relative frequencies of −4.2 (1e), 64.2 (2e), 109.8 ($3a_1$), and 128.8 cm^{-1} (4e) and in combination with the skeletal modes.

Barriers can be extracted from fits of these levels using a particle-in-a-ring basis set with a potential of the form[12]

$$V = \frac{V_3}{2}[1 - \cos(3\theta)] + \frac{V_6}{2}[1 - \cos(6\theta)] + ...$$

Diagonalization yields energy levels in the order $0a_1$, 1e, 2e, $3a_2$, $3a_1$, 4e, 5e, ..., where the levels are labeled according to the particle-in-a-ring quantum number and the symmetry under the G_6 molecular symmetry group.[13] The torsional selection rule for electronic transitions is like-symmetry to like-symmetry. The a_2 levels are typically not observed in jet spectra because the lowest a_2 levels usually are not populated. Barriers of V_3'' = 28 cm^{-1} and V_3' = 150 cm^{-1} were reported by van Zee *et al.*[2] It should be noted that there could be a small (<5 cm^{-1}) V_6 component to both barriers. With the exception of the peak at 40 cm^{-1}, the low-frequency transitions have been assigned. Work in our laboratory on eight different substituted stilbenes indicates that this transition is only present in methylated species and is therefore likely to be a combination band involving a torsional level. We assign the 40 cm^{-1} transition (marked with a star in Figure 7) as the 1e level of 37^1_0, which is symmetry allowed but should be weak. We suspect that it borrows intensity from the origin's 2e level via a Fermi resonance and angular momentum coupling.

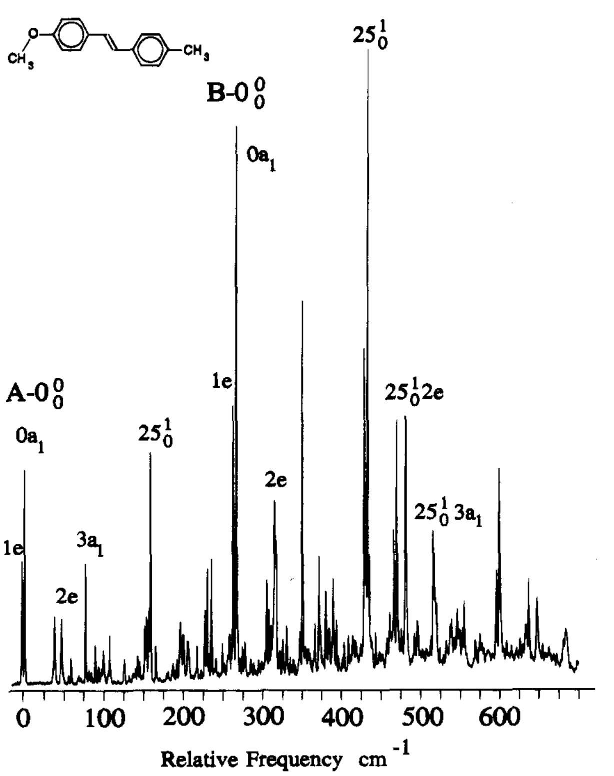

Figure 8. Fluorescence excitation spectrum of *p*-methoxy-*p*′-methyl-*trans*-stilbene (MoMeS). Two origins are observed as in methoxystilbene, and low-frequency methyl torsional transitions appear due to the ring CH_3 as in methylstilbene.

***p*-Methoxy-*p*′-methyl-*trans*-stilbene.** The *p*-methoxy-*p*′-methyl-*trans*-stilbene (MoMeS) excitation spectrum is shown in Figure 8. Readily apparent are two origins separated by 266 cm^{-1}, similar to the case for MoS. Each origin displays a methyl torsional splitting similar to that observed in MeS. The splitting and additional low-frequency torsional structure are readily assigned as being due to the ring methyl torsion not the CH_3 in the methoxy group. This structure was absent in the MoS spectrum. Figure 9 shows an expanded view of the low-frequency region for each conformer with the B origin placed under the A origin for comparison purposes. The B conformer

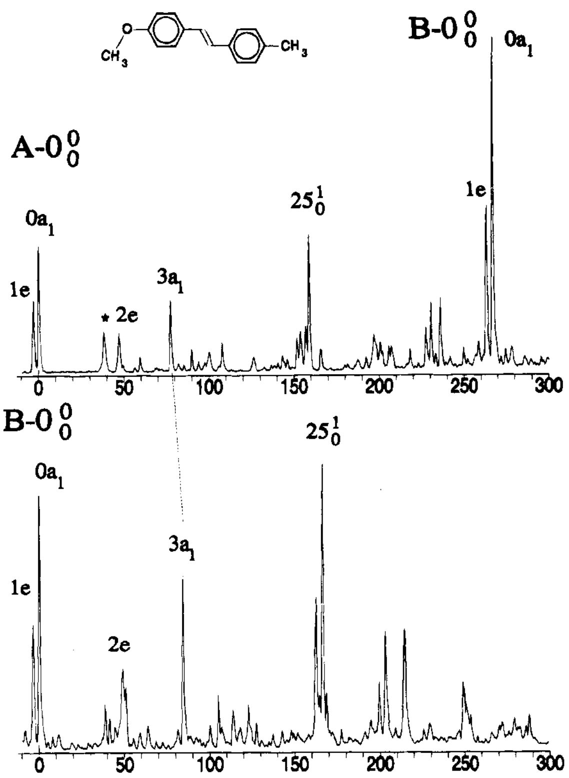

Figure 9. Comparison of the low-frequency portion of the FE spectra for the two conformers of methoxymethylstilbene. Note the higher $3a_1$ frequency for the B conformer (bottom), indicating a higher methyl barrier for that species. The starred transition is 37_0^1 1e, which has gained significant intensity compared to methylstilbene via a Fermi resonance with the 2e level.

spectrum contains higher vibronic levels of the A conformer. The methyl torsional peaks ($0a_1$, 1e, 2e, $3a_1$) for each conformer are labeled, and the assignments were confirmed in both cases using the DF spectra, representative examples of which are shown in Figure 10. Barriers were fit for both electronic states of both conformers using the above-described method, and the results are presented in Tables 3 and 4. The S_0 barrier for both conformers is $V_3'' = 27 \pm 5$ cm^{-1}. The excited state barrier for the A conformer is $V_3' = 92$ cm^{-1}; the corresponding barrier for the B conformer is $V_3' = 103$ cm^{-1}. Evidence for the higher barrier in the B conformer is readily apparent in the excitation spectrum. The $3a_1$ frequency is above 80 cm^{-1} for the B conformer and below 80 cm^{-1} for the A conformer (Figure 9).

The skeletal modes ν_{24} and ν_{25} have different frequencies in the two conformers of MoMeS, as in the case of MoS. These assignments were also confirmed by DF. Unfortunately, 37_0^2 should appear in a region of the spectrum congested with weak transitions. This, coupled with the very poor S/N for DF from these transitions prevented the assignment of 37_0^2 with any confidence. A weak doublet with the $0a_1$ component at 60 cm^{-1} might appear to be 36_0^2, but this would represent a higher frequency than observed in methoxystilbene. Addition of a methyl group in the *para* position would be expected to lower the frequency of this out of plane ring bend, so we assign the weak shoulder to the red of 2e (at 50 cm^{-1}) as 36_0^2 and assign the 60 cm^{-1} transition as the analog of the 67 cm^{-1} peak in MoS. Other assignments are presented in Table 5.

Discussion

Stilbene was chosen as the parent molecule for these investigations for two main reasons: (1) It has sufficient size such that distant ring substituent effects on methyl barriers have to invoke the π system as opposed to direct steric interaction allowing us to address the origin of methyl barriers.[3-6] (2) The involvement of the π system changes greatly as a function of the electronic state, the S_1 state being more delocalized than S_0. Qualitative pictures of the HOMO and LUMO of stilbene illustrate point 2 (Figure 11). The HOMO is π bonding for the C_e—C_e bond but π antibonding for the C_e—phenyl bonds. The converse is true for the LUMO. The S_1 state, which primarily involves promotion of an electron from the HOMO to the LUMO, causes charge transfer from the C_e=C_e bond to the C_e—phenyl bonds and delocalizes the π density over the ethylenic linkage which connects the two rings. Thus, any effect due to the remote ring, or due to changes in the remote ring, will be larger for S_1 than for S_0. This is illustrated by previous work on *p*-methyl-*trans*-stilbene,[2] which has a small V_3'' barrier of ~30 cm^{-1}, indicating that the positions adjacent to the CH_3

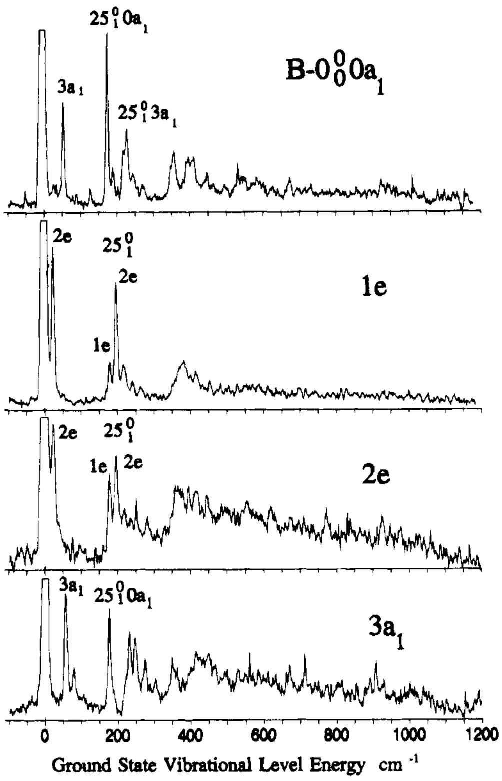

Figure 10. Selected single vibrational level fluorescence spectra used to help assign the excitation spectrum of methoxymethylstilbene.

TABLE 3: Ground State S_0 Methyl Rotor Assignments for *p*-Methoxy-*p*′-methyl-*trans*-stilbene (A: $V_3'' = 27$ cm^{-1}. B: $V_3'' = 27 \pm 5$ cm^{-1})

assignment	A obs (cm^{-1})	B obs (cm^{-1})
2e ← 1e	21	21
$3a_1$ ← $0a_1$	54	52
4e ← 1e	85	85

TABLE 4: Excited State S_1 Methyl Rotor Assignments for *p*-Methoxy-*p*′-methyl-*trans*-stilbene (A: $V_3' = 91.8$ cm^{-1}. B: $V_3' = 103.4 \pm 2$ cm^{-1})

	A conformer		B conformer	
assignment	obs (cm^{-1})	calc (cm^{-1})	obs (cm^{-1})	calc (cm^{-1})
$0a_1$	0.0	0.0	0.0	0.0
1e	−3.2	−3.4	−3.8	−3.8
2e	46.7	47.9	48.8	47.9
$3a_2$		61.8		64.7
$3a_1$	76.8	78.4	84.3	85.1
4e	107.2	106.8		110.9
5e		154		158
$6a_1$		213		217

TABLE 5: S_1 Vibrational Level Assignemtns for the A and B Conformers of *p*′-Methoxy-*p*-methyl-*trans*-stilbene[a]

	A conformer		B conformer	
assignment	freq (cm^{-1})	relative intensity	freq (cm^{-1})	relative intensity
$0_0^0 - 0a_1$	30 517.4	1.00	30 783.4	1.00
1e	−3.2	0.57	−3.8	0.50
$37_0^1 1e$?	38.0	0.35	38.6	0.19
2e	46.7	0.32	48.8	0.34
$3a_1$	76.8	0.56	84.3	0.69
4e	107.9	0.33		
ring tors?	59.4	0.15	60.9	0.09
1e	56.1	0.06	56.6	0.06
$37_0^1 1e$?	99.9	0.09	98.1	0.03
2e	105.0	0.06	108.9	0.10
$3a_1$	135.4	0.07	144.4	0.09
$72_0^1 - 0a_1$	154.2	0.31	169.0	0.24
1e	150.5	0.28	165.2	0.23
$37_0^1 1e$?	193.4	0.13		
2e	200.5	0.33		
$3a_1$	234.4	0.17		
$25_0^1 - 0a_1$	158.7	1.07	166.6	1.14
1e	156.8	0.37	162.7	0.64
$37_0^1 1e$?	196.6	0.32		
2e	205.2	0.22	214.4	0.52
$3a_1$	235.4	0.59	252.8	0.29
$24_0^1 - 0a_1$	230.4	0.53	203.5	0.47
1e	227.2	0.35	199.9	0.28
2e	278.9	0.22	252.5	0.15
$3a_1$	309.0	0.35	290.1	0.15
$25_0^2 - 0a_1$	318		335	0.39
1e			331	0.21
2e			382	0.16
$3a_1$			420	0.11
$25_0^1 24_0^1 - 0a_1$	390		372	0.19
1e			368	0.12
$25_0^3 - 0a_1$			502	0.14
1e			498	0.08

[a] Origin frequencies are reported as absolute (±15 cm^{-1}). Other frequencies are relative to the respective origin.

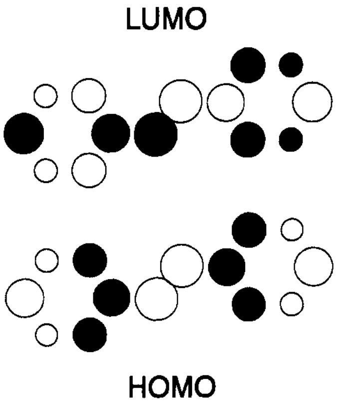

Figure 11. Highest occupied and lowest unoccupied molecular orbitals of *trans*-stilbene calculated using the AM1 hamiltonian showing only the top lobes of the p orbitals. Note the change in the ethylenic and C_e−phenyl π bond characteristics in going from the HOMO to the LUMO.

are inequivalent (otherwise a sixfold barrier would be observed[1]) in the S_0 state. This inequivalence is due to a difference in π densities on either side of the CH_3 rotor axis. The barrier increases fivefold in S_1 to 150 cm^{-1}, indicating a much greater inequivalence in the excited state owing to the off-axis (with respect to the CH_3) position of the remote ring. We speculate that this inequivalence is caused by a weak bonding interaction in the LUMO between the 2 position of the ring and the distant ethylenic carbon, 3 atoms away. This would make the *cis* side of the ring, with respect to the C=C, slightly higher in electron density. This should be a subtle effect, but we do not believe that semiempirical calculations correctly illustrate the magnitude of this inequivalence.

Substitution at the *para* position of the remote ring with the strongly electron donating NH_2 reduces the asymmetry in the vicinity of the CH_3 in the S_1 state. This is because donation into the π electron deficient side occurs more readily than into the electron rich side. This occurs dramatically in the delocalized S_1 state but not so in the localized S_0 state. The S_0 barrier remained ~30 cm^{-1}, but the S_1 barrier was lowered by nearly a factor of 3 to 55 cm^{-1} with amino substitution.

Methoxy substitution is expected to reduce the methyl barrier relative to MeS by donating more density into the electron deficient site adjacent to the CH_3, thereby reducing the π density difference. This should only happen appreciably in the delocalized S_1 state and should occur less efficiently than in *p*-amino-*p*′-methyl-*trans*-stilbene (AMeS) owing to the weaker donating character of methoxy as compared to the amino group. The ~100 cm^{-1} barrier in MoMeS is indeed intermediate to the 150 cm^{-1} barrier for MeS and the 55 cm^{-1} barrier in AMeS, just as the model would predict. This provides strong evidence that π electron interactions are very important in determining CH_3 barriers and that the qualitative model presented is reasonable.

Conformer Differences. The stable conformers display significant differences in their methyl barriers, 92 and 103 cm^{-1} for A and B, respectively. They also display significant differences in the low-frequency ring modes. While the methoxy conformation could affect the reduced mass for some of these modes, we believe the differences in the S_1 state are primarily due to *electronic* differences and the resulting variation in effective force constants. If we first consider ν_{37} in MoS, the methoxy orientation should not have a large effect on the reduced moment of inertia for ring torsion about the *para* axis. Yet, A-37_0^2 has a frequency of 91.5 cm^{-1}, which is appreciably larger than the 85.2 cm^{-1} observed for B-37_0^2. This mode is very sensitive to the C_e−phenyl bond order. The frequency difference implies greater bond order, and more delocalization, for the A conformer than for B. This, in turn, would seem to imply that the methoxy is a better electron donor when its orientation corresponds to that of the A conformer. This assertion is supported by two other pieces of data. The 24_0^1 frequency is higher for the A isomer, as expected for the C_e−C_{Ph}−C_{Ph} bend as the C_e−C_{Ph} bond order increases. Furthermore, the origin of the A conformer lies to the red, as expected for greater π electron delocalization.

The second point requires some elaboration. The lower transition frequency of A is probably predominantly due to a lower S_1 energy for A. We expect the ground state energies for the two conformers to be very similar owing to the lack of delocalization in the ground state. Anisole,[11] for example, only displays one conformation. The two sides of the benzene ring itself are symmetrically equivalent, and interaction between the lone pairs on the methoxy and the π system should be identical for the two conformers. Substitution in the *para* position will create two planar conformers only if the substituent and the parent molecule lack *para* axis symmetry. The energy differences of the two conformers will depend on how electronically different the two sides of the *para* axis in the parent molecule are. MeS has $V_3' \cong 30$ cm^{-1}, indicating that the S_0 state has some π asymmetry in the ring but that it is relatively small. Thus, the difference in energies of the two planar methoxy conformers caused by the interaction of the lone pair with the different π densities will be correspondingly small. This is supported by AM1 calculations which yield a small (<50 cm^{-1}) energy difference for the two planar conformations and a barrier of ~600 cm^{-1} for the perpendicular configuration. However, the π asymmetry increases dramatically in S_1, and so, too, should the conformational energy difference. Thus we expect the transition energy difference to be predominantly due to the S_1 conformational energy difference, and the lower energy conformer is stabilized by greater delocalization of the methoxy lone pair over the stilbene π system. Thus, the lower energy conformer will most likely have the lone pair *cis* to the electron poor side of the ring. This would place the methoxy *cis* to the electron *rich* side, which, as stated above, we suspect is *cis* to the double bond. This predicts the *syn* conformer to be the lower frequency conformer. However, this assignment should be treated as speculative.

Having established that the lower frequency conformer is likely the better electron donor, our model predicts a lower methyl barrier for that isomer of MoMeS. This, in fact, is the case. The A conformer barrier is lower than that of the B conformer by 11 cm^{-1} (~10%). The sensitivity of the methyl barrier to substitution ten atoms away, and the sensitivity to that substituent's **conformation**, strongly supports the validity of using methyl barriers as a probe of excited state π electron densities.

Torsional Interactions. The transition at ~40 cm^{-1} in MeS and MoMeS has no analog in tS or MoS. Initially, it seems reasonable to assign this peak to some motion of the CH_3 group because the transition only appears when a methyl group is present. However, the torsional transitions of the methyl are accounted for and 40 cm^{-1} is too low a frequency for any functional group bends or stretches of the CH_3. Careful backing pressure studies have ruled out assignment as a hot band. This leaves the possibility that the 40 cm^{-1} transition is due to a stilbene vibration that is either greatly shifted in frequency or given allowed character by the presence of the methyl group. Of the stilbene modes, only three are likely to have such a low frequency: ν_{36}, ν_{37}, and ν_{48} all of which are out of plane vibrations.[7,8,10] If we assume that ring torsions are unlikely to tunnel due to their large mass, MeS and MoMeS are G_6 symmetry molecules and out of plane vibrations have a_2 symmetry. The transition in question for each molecule lies at nearly the correct frequency for the 1e level of 37^1_1, which would have e × a_2 = e symmetry and be accessible from the 1e level of the ground state. Strong evidence that the e torsional levels in out of plane modes have allowed character was presented by this group and collaborators for 5-methylindole.[14] In that molecule's spectrum, a whole progression of e levels (with a_1 levels absent) was observed, although the specific out of plane mode involved could not be identified.

In the methylstilbenes we can assign the out of plane mode for which only "e" torsional levels are observed at 40 cm^{-1} due to the known two-quanta frequency of ν_{37}'' and because we expect strong interaction between the methyl and ring torsions. This should result from the phenyl most directly dictating the CH_3 potential and from their common axis of internal rotation which should induce angular momentum coupling.

If we consider what happens to the CH_3 group during the ring torsion, it is straightforward to understand how the modes interact. First, we will consider the limiting case of the ring flipping by 180°, where the methyl just "follows" the ring. This is in one sense no motion of the *methyl* because its internal coordinates should be referenced to the attached ring, which most directly determines its potential. Since the CH_3 groups in MeS and MoMeS have V_3 barriers, the ring flip will take the methyl from a minimum energy conformation (eclipsed on one side and referenced as *syn* or *anti* to the *ethylene*) to a maximum energy conformation (eclipsed on the opposite side). Hence the minimum energy path that rotates the phenyl by 180° must rotate the methyl by 60° or 120°. Conversely, torsion of the methyl should induce motion of the ring via this mechanism. Assignment of a $37^1_0\,3a_2''$ cross-combination band in previous work on MeS[2] supports the idea that these motions couple and cause allowed character in what should be extremely weak combination bands.

It is also interesting to note that the intensity of the ~40 cm^{-1} band is low in MeS (Figure 7) and is strong in MoMeS, where it has intensity nearly equal to that of the 2e band (Figure 9). Owing to the lower barrier in MoMeS, the 2e level lies much closer to the 37^1_0 1e level than in MeS, and the cross combination has significantly greater intensity. This is suggestive of a Fermi resonance between these two levels with the coupling mechanism being angular momentum coupling as described above. Preliminary work on other p'-substituted *p*-methyl-*trans*-stilbenes supports this view.

Another low-frequency transition which might be allowed due to torsional interaction is the 67 cm^{-1} transition in MoS (59.4 cm^{-1} in MoMeS), which does *not* appear in *trans*-stilbene or MeS. Again it is tempting to assign this transition to a functional group vibration of the methoxy substituent. However, preliminary work in our laboratory indicates that the same transition is observed at the nearly identical frequency in *p*-hydroxystilbene. The differences in reduced mass between OCH_3 and OH dictate significant differences in functional group vibrational frequencies, so again it appears that the transition is a stilbene vibration that is modified by the presence of the methoxy group. Because of the low frequency of the peak, ν_{36}, ν_{37}, and ν_{48} are again the likely candidates. A unique feature of this transition is that it only appears in substituents that lack *para* axis symmetry. This suggests that *ring* torsions may be involved because the substituent can spoil the twofold symmetry of the phenyl rotor.

Here, it is useful to consider the ring torsion surface qualitatively pictured in Figure 12 and similar to that of Laane and co-workers.[9] There are four equivalent minima in tS itself, corresponding to the planar ring conformations. The horizontal axis in the potential is the torsional coordinate for a single ring; the vertical axis is the torsional coordinate of the other ring. A second axis system, rotated by 45° relative to the first, corresponds to moving both rings with one axis being ν_{37} and the other ν_{48}. For phenyl torsions in tS, the ν_{37} and ν_{48} description is more appropriate. However, it is easy to imagine that if we substituted one phenyl with several very large groups, the vibration would tend to localize in the less hindered ring and the localized torsional axis system would more closely reflect reality. This, of course, could be expressed as a linear combination of ν_{37} and ν_{48}. Short of this local mode extreme the two normal modes would appear to start mixing. In the S_1 state of MoS, we know that if we flip the anisole ring by 180°, we will convert to a different methoxy conformer which differs in energy by ~270 cm^{-1}. This causes one pair of minima in the potential surface to differ in energy from the other two and requires more local torsional character for a more accurate description. Laane and co-workers[9] have modeled the potential in the S_1 state of tS and estimate a barrier of ~3000 cm^{-1}. This places the difference in minima at ~10% of the barrier height. This is not enough to cause truly localized vibrations at low energies, but it probably is sufficient to cause noticeable ν_{37} and ν_{48} mixing. While we cannot yet identify the appropriate description of this level, we strongly suspect that this mechanism is responsible for the observed transitions at 67 and 59.4 cm^{-1} in the A conformers of MOS and MoMeS, respectively.

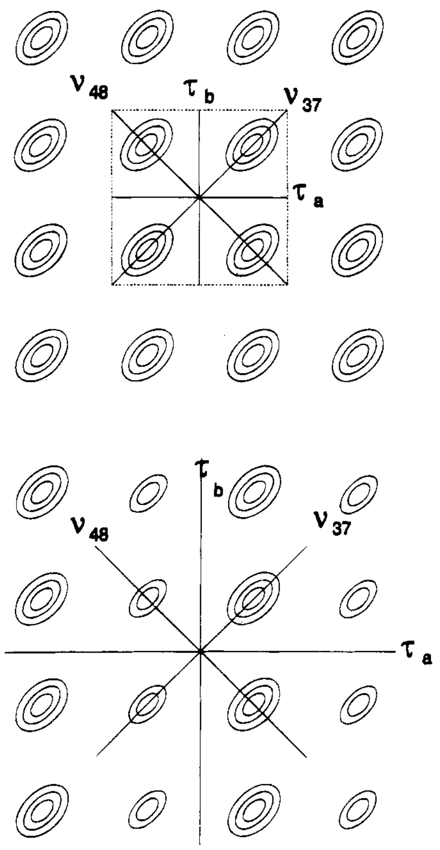

Figure 12. "Cartoon" depiction of how the S_1 stilbene ring torsional surface (top) should be modified by methoxy substitution (bottom) owing to the different energies of the methoxy conformations. The minima occur when the rings are coplanar with the ethylenic group; τ_a and τ_b are local coordinates of an individual ring torsion; ν_{37} and ν_{48} are the normal modes involving torsion for both rings as shown in Figure 3. Torsion of the methoxy-substituted ring interconverts methoxy conformers and results in a different energy minimum. This lowers the symmetry of the surface and may result in new transitions in the spectrum.

One final anomaly that is worth mentioning occurs in the spectrum of the B conformer of *p*-methoxy-*p*′-methyl-*trans*-stilbene. The methyl torsional progression of the origin has relative intensities that correspond nicely with those calculated for a 60° conformational change. Progressions based on 25^1_0 and high-frequency fundamentals and combination bands show similar relative intensities for all the torsional members *except* $3a_1$, which is markedly reduced in intensity and displays some broadening. It appears that above 250 cm^{-1} the $3a_1$ level acts as a doorway state for a nonradiative process. What is intriguing is that this is not true for a_1 symmetry levels in general ($0a_1$ levels above 250 cm^{-1} do not show this behavior) and that it occurs only for the B conformer. While the available data do not provide sufficient information to elucidate the nature of the dynamical process, the nature of the levels involved suggests some possibilities. We have seen that the methoxy group modifies the ring torsional surface and that the higher energy conformer in the S_1 state, the so-called B conformer, will have a higher local minimum. Thus, the B conformer is ~270 cm^{-1} higher on the ring torsional surface than the A conformer. This could account for the observation of the doorway state above 250 cm^{-1} in *only* the B geometry. The special nature of the $3a_1$ level might be due to the fact that it is the only CH_3 torsional level above the methyl barrier with a suitable Franck–Condon factor to be observed. Once above the barrier, the CH_3 angular momentum may couple more efficiently and induce ring torsions and may also open a lower energy pathway along the complicated methyl, phenyl, methoxy torsional surface.

This mechanism could also enhance the well-known, and extensively studies, *trans–cis* isomerization of the stilbene backbone.[15] In tS, experimental data suggest that this isomerization has a threshold at ~1200 cm^{-1} of excess energy.[16–18] Recent theoretical studies of Frederick and co-workers[19] strongly implicate the *ring* torsions as playing an important role in the process, a logical result given that the rings are twisted with respect to the ethylenic plane in the *cis* form. While the 270 + 250 cm^{-1} barrier provided by the B conformer's $25^1_0 3a_1$ level may seem small compared to the ~1200 cm^{-1} barrier in tS, it should be remembered that in tS the process was statistical. The ring torsions are particularly low frequency and may not couple efficiently to the other modes. Thus the energy required for a statistical process may exceed the barrier because of poor coupling into the relevant mode. By modifying the ring torsional surface via methoxy substitution, and accessing the multiple torsional surface as suggested above, energy may be more efficiently deposited into the active modes.

Summary and Conclusions

In *para*-substituted *p*′-methylstilbenes, the excited state methyl barrier is sensitive to the nature of the substituent 10 carbons away. Much smaller effects are observed in the less delocalized ground state, providing nearly conclusive evidence that π electron effects are the dominant factor in determining threefold methyl barriers. The barriers correlate with the expected π density difference in the two positions adjacent to the CH_3-substituted carbon. In *p*-methyl-*trans*-stilbene the asymmetry in the π density is primarily due to the remote ring not being coaxial with the methyl rotor. However, without delocalization over the ethylenic system, the asymmetry caused by the remote ring cannot be transmitted to the toluene ring yielding low barriers in the non-delocalized S_0 state. Substitution with the electron-donating methoxy group reduced the S_1 barrier relative to that of *p*-methylstilbene[2] but not as low as that of *p*-amino-*p*′-methylstilbene.[1] This supports the hypothesis that donating groups more readily increase density at the π deficient side of the methyl rotor, reducing the asymmetry in π density. Withdrawing groups will also decrease the S_1 barrier by withdrawing more density from the π rich side and should also reduce the S_1 barrier relative to that of MeS.

In addition to being sensitive to the substituent, it was observed that the methyl barrier is sensitive to substituent conformation in *p*-methoxy-*p*′-methyl-*trans*-stilbene. A red-shifted origin and a larger ring torsional frequency (both evidence of greater delocalization) indicate that the lower frequency methoxy conformer denoted as A in this work is slightly stronger electron donor. That conformer has a lower methyl barrier consistent with the model, indicating great sensitivity of methyl barriers to subtle changes in the π system.

Low-frequency transitions that appear in a number of substituted stilbenes, but not in stilbene itself, could not be attributed to vibrations of the substituent and strongly suggest that substitution significantly modifies ring torsions in stilbene. More complete understanding of these processes will require a careful nonrigid group theoretical treatment and perhaps computational modeling of angular momentum coupling between the ring torsion and substituent motion.

This work validates the use of methyl barriers as a probe of π electron effects in excited states of moderately sized organic molecules. These methods can potentially yield important data for efforts aimed at improving excited state calculations.

Acknowledgment. This work was supported by the NSF through Grant CHE-9120194. We also thank Brian Metzger for synthesizing the *p*-methoxy-*p*′-methyl-*trans*-stilbene.

References and Notes

(1) Yan, S.; Spangler, L. H. *J. Phys. Chem.* **1995**, *99*, 3047.

(2) Spangler, L. H.; Bosma, W. B.; van Zee, R. D.; Zwier, T. S. *J. Chem. Phys.* **1988**, *88*, 6768.

(3) Hehre, W. J.; Pople, J. A.; Devaquet, A. J. P. *J. Am. Chem. Soc.* **1976**, *98*, 664.

(4) Dorigo, A. E.; Pratt, D. W.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 6591.

(5) Moss, D. B.; Parmenter, C. S.; Ewing, G. E. *J. Chem. Phys.* **1987**, *86*, 51.

(6) Lu, K. T.; Weisshaar, J. C. *J. Chem. Phys.* **1993**, *99*, 4247.

(7) Suzuki, T.; Mikami, N.; Ito, M. *J. Phys. Chem.* **1986**, *90*, 6431.

(8) Spangler, L. H.; van Zee, R. D.; Zwier, T. S. *J. Phys. Chem.* **1987**, *91*, 2782.

(9) Chiang, W.-Y.; Laane, J. *J. Chem. Phys.* **1994**, *100*, 8755.

(10) Warshel, A. *J. Chem. Phys.* **1975**, *62*, 214.

(11) Breen, P. J.; Bernstein, E. R.; Secor, H. V.; Seeman, J. I. *J. Am. Chem. Soc.* **1989**, *111*, 1958.

(12) Flygare, W. H. *Molecular Structure and Dynamics*; Prentice Hall: Englewood Cliffs, NJ, 1978.

(13) Bunker, P. R. *Molecular Symmetry and Spectroscopy*; Academic Press, New York, 1979.

(14) Sammeth, D. M.; Siewert, S. S.; Callis, P. R.; Spangler, L. H. *J. Chem. Phys.* **1992**, *96*, 5771.

(15) For reviews see: (a) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415. (b) Saltiel, J.; Sun, Y.-p. In *Photochromism Molecules and Systems*; Durr, H., Bouas-Laurent, Eds.; Elsevier: Amsterdam, 1990. (c) Hochstrasser, R. M. *Pure Appl. Chem.* **1980**, *52*, 2683.

(16) Zwier, T. S.; Carrasquillo, E.; Levy, D. H. *J. Chem. Phys.* **1983**, *78*, 5493.

(17) Majors, T. J.; Even, U.; Jortner, J. *J. Chem. Phys.* **1984**, *81*, 2330.

(18) Syage, J. A.; Felker, P. M.; Zewail, A. H. *J. Chem. Phys.* **1984**, *81*, 4706.

(19) Vachev, V. D.; Frederick, J. H.; Grishanin, B. A.; Zadkov, V. N.; Koroteev, N. I. Submitted to *J. Phys. Chem.*

JP950143L